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## FRILL-LIKE DEFECT IN GLAZES IN THE CONTEXT OF SYNERGISM

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The behavior of the glaze layer deposited on a ceramic sample is considered from the standpoint of nonequilibrium thermodynamics beginning with the moment of slip deposition up to the birth of the melt. The significance of a combined approach to the study of this process is demonstrated and methods for the control of the macrostructure of the coating thus formed are proposed.

A defect known as “frill-like glaze” is encountered in the glazing of ceramic articles. It consists in spontaneous disturbance of the continuity of the glaze layer. The glaze aggregates in drops, and some portions of the article surface remain unglazed. The disturbance of the continuity of the glaze layer can be caused by different reasons: inadequate chemical composition of the glaze, its too high dispersion (overmilling), a too thick layer of glaze, existence of surface sites not wetted by slip, gas emission from samples, etc. [1]. The variety of possible reasons hinders the identification of a specific reason for this defect and impedes the search for a method for its elimination.

The purpose of the present study is to analyze of the process of formation of the “frill defect” in the context of synergism, which, in our opinion, should facilitate understanding of the causes for this phenomenon and outline ways for controlling the process.

The thermodynamics of nonequilibrium processes recognizes what is known as dissipative structures, i.e., the physical systems emerging as a result of a highly nonequilibrium process which have some common properties [2]. These properties include the openness and the macroscopic nature of the system, the possibility of being described by nonlinear mathematical equations allowing for a variation in the solution symmetry. All this evidence is present in the description of the “frill” defect. We are dealing with an open system; the “frill” is a macrodefect; and the diffusion processes which accompany spreading of the glaze are nonlinear. The frill defect changes the topology of the system: instead of a continuous layer, the glaze aggregated in drops.

The dissipative structures are the result of a nonequilibrium process which has passed a bifurcation point, i.e., the moment of indefinite stochastic behavior of the system. Glaze frilling is a typical bifurcation process, when the system acquires increased sensitivity both to internal fluctua-

tions and external disturbances. Therefore, in the moment of glaze spilling, i.e., at the point of bifurcation, the future evolution of the system in principle cannot be exactly predicted, since it is determined by the actions of unpredictable signals (noises). However, if the evolution is made predictable by using certain controlling actions, it will mean the elimination of the bifurcation point.

Since both internal and external controlling actions can affect the behavior of the system (the glaze layer), to make the evolution of the system predictable the controlling effects should exceed the noise level (internal fluctuations and external disturbances) [3].

We needed to select a glaze and a ceramic substrate which would regularly produce the frill effect. It was planned to study the behavior of the glaze melt deposited on ceramic samples in relation to such factors as the state of ceramic surface, the thickness of the glaze layer, and the drying and second firing parameters.

Preliminary experiments revealed that majolica glaze No. 4518 produced by the Dulevskii Paint Factory when deposited on samples made of Skorotovskoe clay (Moscow Region) regularly produced the frill effect. In order to investigate this defect, ceramic samples 60 × 40 × 10 mm in size were prepared. The coefficient of thermal linear expansion (TCLE) of the sintered samples was  $5.4 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ . The properties of the ceramic samples are listed in Table 1.

TABLE 1

Sample	Firing temperature, $^\circ\text{C}$	Fire shrinkage, %	Open porosity, %
1	900	5.5	27
2	950	6.1	25
3	1000	6.5	24
4	1050	7.2	21
5	1100	8.5	11

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The majolica glaze had a softening point of  $585 \pm 30^\circ\text{C}$ , a temperature of drop formation of  $785 \pm 40^\circ\text{C}$ , and a spreading temperature of  $920 \pm 40^\circ\text{C}$ . Its residue on a No. 0063 sieve was 0.079%, and the TCLE was  $5.86 \times 10^{-6}^\circ\text{C}^{-1}$ . The difference in the CTLE of the glaze and the ceramic substrate coated with this glaze did not exceed the permissible level, which precluded formation of crackle in the glaze [4].

A glaze slip whose moisture was 50% was prepared with distilled water. The slip was deposited by pouring or spraying from a pulverizer. The temperature of the second firing was  $1000^\circ\text{C}$  with 0.5 h holding. The samples were cooled together with the furnace. The thickness of the glaze layer was determined on an optical microscope. The optical microscope was used as well to evaluate the glaze layer structure and the ratio between the glazed and unglazed surface areas.

The samples were covered with slip whose thickness after drying was about  $150\ \mu\text{m}$ , and then dried and fired. In all cases the frill effect was visible in the form of glaze drops of different shapes and sizes. Optical microscopic studies revealed that the glaze disintegrates into fragments limited by cracks as early as the drying phase. The size of the fragments depends on the drying conditions (the degree of nonequilibrium of the process) and the sample porosity (the state of the sample surface). The obtained results are represented in Table 2.

It is known that an increase in the degree of nonequilibrium is followed by a decrease in the size of structural elements [5, 6]. By contrasting the data in Table 2, it is seen that an increase in the drying rate of the deposited glaze layer is equivalent to an increase in the degree of nonequilibrium of the process, causes a certain decrease in the size of the fragments and the width of the cracks between the fragments, and also produces a slight decrease in the glazed surface area.

It is much more difficult to trace the effect of the state of the sample surface. Samples 3 in Table 2 exhibit the maxi-

mum size of the glaze fragments and the cracks between them. With an increase in open porosity (Samples 1 and 2), the thickness of the slip-deposited layer increases. However, since the porosity is high, the drying rate in this case remains sufficiently high. Apparently, the degree of the process nonequilibrium is the determining factor, while the increase in the layer thickness and, accordingly, its rupture strength does not play a determining role in this case. Moreover, an increased surface roughness produces stress concentrators in the drying layer, which reduces its rupture strength.

A decrease in the porosity of the substrate samples (from sample 3 to sample 5) produces a decrease in the size of the fragments and the cracks between them. With a decrease in porosity, the thickness of the glaze layer deposited within the same time decreases. The thin layer dries sooner, which increases the degree of nonequilibrium of the process. With a decrease in the layer thickness, the effort required to break it becomes lower, which facilitates the disintegration into smaller fragments.

An increase in the layer thickness was achieved by repeated deposition of glaze layers after they were dried. As the thickness of a dry glaze layer changed from the minimum value ( $150\ \mu\text{m}$ ) to  $350\ \mu\text{m}$ , a continuous, although uneven glaze layer was formed, which exhibited an increased amount of defects in the form of pinholes and pimples. With a layer thickness equal to  $350 - 500\ \mu\text{m}$ , the frill effect appeared, and the size and height of emerging drops sharply increased. With a further increase in the thickness of the dry glaze layer, its structure changed insignificantly.

With an decrease in the thickness of the glaze layer, the effort required for its rupture decreases, but the rate of drying and, consequently, the degree of the process nonequilibrium increase. It apparently restricts the glaze capacity for relaxation (through plastic deformation). Numerous microdefects emerge in glaze, which produce relaxation of tensile stress and, therefore, decrease the propensity of the glaze layer for disintegration into large fragments with macrocracks along their boundaries. This agrees with the data in Table 2 for samples 4 and 5.

An increase in the thickness of the glaze layer increases the effort needed for its rupture, which requires more substantial stresses for the layer to disintegrate into fragments and, consequently, an increase in the fragment size, and results in the emergence of the frill defect.

The performed experiments give reason to assume that the cause for the frill defect in the analyzed glazes consists in the local compactions of the glaze layer, the basis for which is laid in the stage of slip deposition and drying. Due to the effect of the structure inheritance, local compactions can have a determining effect on the evolution of the structure [7]. The nonuniform air shrinkage caused by the nonuniform density of the glaze layer results in spontaneous disintegration into fragments (dissipative structures). An increase in the thickness of the deposited slip layer facilitates an increase in the size of the fragments. Subsequently in heat

TABLE 2

Sample	Macrostructure of the glaze layer		Surface area covered with glaze, %
	fragment size, $\mu\text{m}$	crack size, $\mu\text{m}$	
<i>After drying at a temperature of 25°C</i>			
1	5300	35	43
2	5900	90	48
3	6100	100	52
4	5600	60	54
5	4600	20	76
<i>After drying at a temperature of 80°C</i>			
1	4900	25	44
2	5300	60	49
3	5500	80	57
4	5400	40	69
5	4500	20	80

treatment the fragments start shrinking (until the beginning of glaze spreading). The glaze primarily aggregates in drops in order to decrease its outer surface (a sphere). Furthermore, as the temperature increases, the area of the surface wetted by the drop insignificantly increases, and the drop is not able to cover all of the initial surface. The result is determined by the mutual relationship between the surface tension force and the relatively weak wetting force. The surface tension force strives to agglomerate the fragments in drops with the minimum outer surface, and the wetting force strives to cover the maximum surface of the substrate. An accelerated heating procedure can only intensify the manifestation of the tendency to the frill defect which is already inherent (due to the chemical and granulometric composition of the glaze and the physicochemical state of the surface).

Therefore, the frill defect can be regulated only by identifying the group of factors responsible for its appearance and controlling the geometry of the dissipative structures formed during the deposition and drying of the glaze layer. The geometry of the dissipative structures can be controlled at the level of external energy disturbances or by restricting the internal fluctuations to the limits of the fragments prescribed. The larger the fragment, the larger the unglazed spaces dividing the fragments.

Some attempts were made to eliminate the frill defect by introducing polyvinyl alcohol (PVA) and carboxymethyl cellulose into the slip. The use of PVA or carbomethyl cellulose perceptibly repressed the formation of frill. At low temperatures, the plasticity of the polymers facilitates the relaxation of the emerging stresses and impedes the formation of sufficiently large fragments and cracks. However, the polymers lose their plasticity in heat treatment. Apparently in these conditions the continuing shrinkage produces considerable stresses which cause disintegration of the layer into smaller fragments. The size of these fragments, as a rule, is smaller than the size of the fragments formed without the use of organic binders and PVA.

In order to prevent the frilling effect, the fragment should be reduced to the optimally small size. The optimum-size fragment is a fragment which can be accepted by the system as the main element for a dissipative structure [3]. If the average size of the fragment is below the optimum size, the system will resume developing larger fragments as dissipative structures. If the size is significantly larger than the optimum, the system itself can split them into fragments with an average size below the optimum. However, in such an event, part of the fragments will retain their larger than optimum size, which will result in the frill defect.

The optimally small size is one that makes the unglazed sites so small that a slight increase in the wetting area after the glaze spreads will result in the healing of the unglazed areas. This is due to the fact that shrinkage is proportional to the size of the fragment, and spreading (i.e., an increase of the size with respect to the previous boundary) is a nearly constant value.

In order to verify the above hypothesis, we used preliminary splitting of the glaze layer into fragments of certain sizes. Metallic sieves of different sizes wetted in oil were applied to a freshly deposited and still moist slip layer and pressed to it to get an imprint. The slip layer was split into squares. Next, the samples were dried and fired at a temperature of 1000°C. The results are given in Table 3.

It should be noted that the samples which did not have the frill defect after the second firing at a temperature of 1000°C retained the relief imprint of the sieve on their surface. Further heat treatment at a higher temperature made the imprint disappear. Addition of PVA to the glaze slip caused an increase in the optimum size of the fragment. This can be explained by the fact that the shrinkage of the fragments in the course of heat treatment decreased, predominantly in the directions parallel to the coated surface. The decrease in shrinkage produces a decrease in the size of the cracks between the fragments, and the cracks heal as the glaze spreads. The high porosity in samples 1 determined the speedy removal of moisture and the loose packing of the particles both in the presence and absence of PVA. The speed of water removal in samples 3 and 5 is lower in the presence of PVA than without PVA. Taking into account the decrease in friction due to the addition of PVA, this allows the glaze particles to develop a denser layer which has a lower shrinkage in heat treatment. The optimum size of the fragments in the presence of PVA increases in samples 3 and 5 up to 1000  $\mu\text{m}$ . Thus, the optimum size of the fragments is primarily related to the size of the unglazed crack between the fragments, which emerges in heat treatment.

The synergistic approach makes it possible to outline the possible ways of regulation of the size of the fragments. Part of these methods are traditionally used for prevention of cracks in fine ceramic articles [8]: introduction of grog additives, variation of drying conditions, use of surfactants, control of the heat carrier moisture, etc.

The application of grids of different dimensions to a wet glaze layer makes it possible to determine experimentally the optimum size of the block. Knowledge of the optimum size of the fragment makes it possible to control the size of the

TABLE 3

Sample	Size of sieve cell (fragment), $\mu\text{m}$			
	300	500	1000	2000
<i>Fragment without PVA</i>				
1	Frill	None	Frill	Frill
3	The same	The same	The same	The same
5	"	"	"	"
<i>Fragment with additive of 1.7 wt.% PVA</i>				
1	Frill	None	Frill	Frill
3	The same	Frill	None	The same
5	"	The same	The same	"

fragments in the intermediate raw product and to predict the frill defect before the second firing. If the size of the fragments formed in the dried glaze layer is close to the optimum one, the appearance of frill is unlikely.

Control of the frill effect can be reduced to control of the size of the fragments, or more exactly, the width of the unglazed cracks between the fragments, which is determined by the glaze shrinkage. This is equivalent to elimination of the bifurcation.

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